Research Article

Electrodeposition of Nanometer-Sized Ferric Oxide Materials in Colloidal Templates for Conversion of Light to Chemical Energy

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Colloidal crystal templates were prepared by gravitational sedimentation of 0.5 micron polystyrene particles onto fluorine-doped tin oxide (FTO) electrodes. Scanning electron microscopy (SEM) shows that the particles were close packed and examination of successive layers indicated a predominantly face-centered-cubic (fcc) crystal structure where the direction normal to the substrate surface corresponds to the (111) direction. Oxidation of aqueous ferrous solutions resulted in the electrodeposition of ferric oxide into the templates. Removal of the colloidal templates yielded ordered macroporous electrodes (OMEs) that were the inverse structure of the colloidal templates. Current integration during electrodeposition and cross-sectional SEM images revealed that the OMEs were about 2 μm thick. Comparative X-ray diffraction and infrared studies of the OMEs did not match a known phase of ferric oxide but suggested a mixture of goethite and hematite. The spectroscopic properties of the OMEs were insensitive to heat treatments at 300°C. The OMEs were utilized for photoassisted electrochemical oxidation. A sustained photocurrent was observed from visible light in aqueous photoelectrochemical cells. Analysis of photocurrent action spectra revealed an indirect band gap of 1.85 eV. Addition of formate to the aqueous electrolytes resulted in an approximate doubling of the photocurrent.

1. Introduction

There is an urgent need to find inexpensive and sustainable inorganic materials for converting solar photons into chemical energy. Splitting water with metal oxides and sunlight is a very appealing idea that has caught the attention of scientists for decades [1]. One approach has been to utilize a metal oxide photoelectrode that can photo-oxidize water and provide electrons to a platinum electrode for proton reduction [2]. Shown in Figure 1 is a simplified version of such a cell. To aid in hydrogen gas collection and to prevent O_2 reduction at the platinum electrode the two electrodes can be separated by a salt bridge or porous membrane.

Fujishima and Honda first reported sustained water splitting through this approach with TiO_2 [2]. Unfortunately, the unfavorable band gap of rutile TiO_2 (3.1 eV) resulted in a very low solar conversion efficiency (<1%). Later, other wide band gap metal oxides were shown to work in a

similar fashion [3–5]. Hematite, $\alpha\text{-Fe}_2\text{O}_3$, has a much more favorable 2.2 eV band gap for solar harvesting and therefore absorbs about 40% of the air mass 1.5 solar spectrum [6–8]. Previous researchers found that the energetic position of the valence band edge in hematite is appropriate for water oxidation [9–21]. In fact, iron oxides are amongst the smallest band gap semiconductors that are stable toward oxygen evolution and are certainly the least expensive of them. However, overall charge collection efficiencies from hematite in photoelectrochemical cells has been disappointingly low [6].

Much of the early work on hematite photoelectrochemistry was done in the 1970–1980s; however, recently there have been a few promising reports [22–34]. Poor solar charge collection efficiency was attributed to low minority (hole) diffusion lengths [30]. In other words, photogenerated valence band holes do not efficiently reach the hematite-water interface and primarily recombine in the bulk. In

FIGURE 1: Photoelectrosynthetic cell for splitting water into H_2 and O_2 . The two electrodes can be separated by a physical barrier to aid in gas collection.

principle, this problem can be circumvented with iron oxide electrodes that have architectures tailored towards high surface area and minimal internal volume such that all photogenerated holes reach the solution interface.

New processing techniques that have been developed in the last twenty years may enable the production of semiconductor materials with architectures ideal for charge capture at a solution interface. Colloidal templates offer interesting possibilities in this regard as they could allow ferric oxide structures to be controlled with considerable precision [35, 36]. The average distance photogenerated holes would need to travel to reach the interface can be systematically tuned by varying the size of the colloidal particles used in the template. High surface area, porous materials that can be fine tuned to optimize hole capture at the aqueous interface are expected to be ideal for light harvesting and oxygen evolution in photoelectrosynthetic cells. Furthermore, hole transfer and/or oxidation catalysts, such as RuO_2 and IrO_2 could be included at desired locations within the structure to decrease oxidation overpotentials and improve kinetics [1]. Recently we have initiated experiments to establish whether colloidal templates could be used to fabricate ferric oxide in ordered macroporous thin films. Here we report that this can indeed be accomplished and report the synthesis of ordered ferric oxide electrodes. Photoelectrochemical studies with the templated ferric oxide materials reveal small sustained photocurrents that may be consistent with water oxidation, but the present architecture is not suitable for practical application in photoassisted water oxidation.

2. Experimental

2.1. Materials. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99%), L-ascorbic acid (Aldrich, >99%), NaCl (Mallinckrodt Chemicals, >99.0%), 1-methylimidazole (Aldrich, 99%), polystyrene (PS) microbeads (Polysciences, $0.5 \mu\text{m}$ diameter), ethanol (Aaper Alcohol, anhydrous 200 Proof), NaOH (Fisher, 97.5%), NaCHOO (Aldrich, 99+%), and Na_2SO_4 (EMD, 99.0+%) were used without further purification. Electrolytes for electrodepositions used HPLC grade water; all other solutions used deionized water. Conductive fluorine doped tin oxide glass, FTO (Hartford Glass, $\text{SnO}_2:\text{F}$) and Au evaporated Si wafers were cleaned with water and ethanol prior to electrodeposition.

2.2. Templating. The assembly of the colloidal crystalline template followed literature preparations, described briefly as follows [37, 38]. Sheets of FTO or wafers of gold evaporated on silicon were cut to $4.0 \text{ cm} \times 2.5 \text{ cm}$ dimensions and uses as substrates. They were first sonicated in glass vials with absolute ethanol, rinsed with deionized water, and dried under compressed air. Viton and Teflon o-rings were also rinsed with deionized water and dried under compressed air. The Viton o-ring was placed on the conductive side of the substrate. The Teflon o-ring was placed on top of the Viton o-ring. Both rings were clamped onto the substrate using binder clips. The PS particles were diluted by 1:8 v:v in deionized water and stored at 4°C . Prior to assembly the suspension was sonicated for two minutes. A $170 \mu\text{L}$ aliquot of the diluted PS particle suspension was carefully pipetted onto the substrate and was placed in a humidity chamber at room temperature and 85% humidity. After six days the clamps and o-rings were removed leaving an ordered colloidal crystal template. The substrate was cut to the width of the template yielding a templated electrode $1.0 \text{ cm} \times 4.0 \text{ cm}$, which was stored in a humidity chamber until use.

2.3. Electrodeposition. Ferric oxide was electrodeposited into the colloidal crystalline templates. Electrodeposition was carried out in an Ar purged, septa sealed, three electrode cell with the colloidal crystal template as the working electrode, FTO as the counter electrode, and Ag/AgCl (KCl saturated) as a reference electrode. All potentials are reported with respect to the Ag/AgCl reference ($U_{\text{eq}} = +0.110 \text{ V SHE}$). The electrodeposition solution contained $50 \mu\text{L}$ of 1 M FeCl_2 solution, $150 \mu\text{g}$ of L-ascorbic acid, and 5 mL of a 0.4 M NaCl and 0.1 M 1-methylimidazole electrolytic solution [39]. Ferric oxide was deposited at -0.30 V under a slow purge of nitrogen in the head space until -0.30 C/cm^2 were passed. The film was then immersed in toluene for ten minutes. The electrodeposited ferric oxide adhered to the FTO as an ordered macroporous electrode (OME). The OME were removed from the toluene and stored in sealed glass vials until use. Preparation of the template and electrodeposition onto Au evaporated Si wafers followed the same methods used for OMEs on FTO.

2.4. Characterization. Environmental scanning electron microscope (ESEM) images were taken on an FEI Quanta 200 Environmental SEM at a water vapor pressure of 1.8 kPa. Cross sectional SEM images of colloidal crystalline templates and ferric oxide OME deposited on Au that had been evaporated onto Si wafers were acquired with a JEOL 6700 F Scanning Electron Microscope. The UV/Visible electronic spectra were acquired on a Cary 500. Fourier transform infrared (FTIR) spectra were acquired on a Thermo Nicolet Nexus 670 FTIR with a Smart Golden Gate ATR attachment. X-ray diffractograms (XRD) were acquired on a Philips X'Pert Pro X-ray Diffraction System using Cu-K α radiation. For XRD measurements, the ferric oxide OME was removed from the FTO substrate with a razor blade. All other characterization techniques were acquired on intact ferric oxide OME.

2.5. Photoelectrochemistry. Photocurrent action spectra were recorded with a Keithley 5000 electrometer under short circuit conditions in a custom-built liquid junction Teflon cell with a Pt mesh counter electrode. The electrolyte was 0.1 M NaCl at pH 9.5 adjusted with NaOH. The light source was a 100 W Xe arc lamp (Spectra Physics) attached to a monochromator (Oriel Instruments Corner Stone 1/4 m). Incident irradiances were measured with a UDT high sensitivity silicon diode optometer.

Photocurrents were also measured in a three-electrode arrangement with a BAS CV50-W potentiostat. The working electrode was a ferric oxide OME with a Pt mesh counter electrode and a Ag/AgCl reference electrode. The aqueous electrolytes used were either 0.5 M Na₂SO₄ or 0.1 M NaCHOO/0.5 M Na₂SO₄. In a typical experiment, the applied bias was ramped from 0.0 V to +1.3 V at a scan rate of 2 mV/s. This was then repeated with the ferric oxide OME illuminated with 20 ± 1 mW/cm² of 413.1 nm light from a Continuum Kr ion laser. The photocurrents are reported as the total current measured under illumination minus the dark current.

3. Results

The colloidal crystal templates were prepared by gravitational sedimentation of polystyrene (PS) particles onto fluorine-doped tin oxide (FTO) electrodes. The quality of the crystal was dependent on the particle concentration, temperature, and relative humidity. The conditions used ensured controlled evaporation of the solvent and sufficiently slow sedimentation to result in well-ordered crystals. Faster evaporation rates typically resulted in defects such as cracks or voids that led to large volumes of solid in the replica after deposition. Figure 2 shows SEM images of a typical 4 μ m thick colloidal crystal template formed by this technique. The image shows that the particles were close packed, and examination of successive layers confirmed a predominantly face-centered-cubic (fcc) crystal structure where the direction normal to the substrate surface corresponds to the (111) direction.

Ordered macroporous electrodes (OMEs) of ferric oxide were formed by electrodeposition into the templates at

−0.30 V (Ag/AgCl). The deposition charge of 0.30 C/cm² corresponded to an OME thickness of 2 μ m, in reasonably good agreement with values obtained from cross-sectional SEM images (2.8 ± 0.1 μ m). The PS particles were removed by immersion in toluene that left an orange-red OME on the FTO substrate.

A representative plan view SEM image of a ferric oxide OME is shown in Figure 3(a). The top surface revealed a close packed mesostructure that was a replica of the colloidal crystal template. The domain size was 15–50 μ m and the OMEs were free from cracks or voids. The surface roughness factor, or rugosity, of a 2.8 μ m thick OME was about 25 corresponding to about 6.5 layers of template as seen in the cross-sectional SEM, Figure 3(b).

Attenuated total reflection Fourier transform infrared, ATR-FTIR, spectroscopic characterization of the OMEs were performed, Figure 4. The broad O-H stretch at 3200 cm^{−1} and overtone at 1600 cm^{−1} are diagnostic of adsorbed water [41]. The intensity of these bands decreased after heating the OME at 300°C for 30 minutes. The heat treatment did not significantly change the FTIR spectra of other regions of the spectra.

X-ray diffraction (XRD) analysis of the electrodeposited ferric oxide showed weak intensity and broad angular distribution of the diffraction peaks, Figure 5. Superimposed on this data are the literature values for the diffraction peaks of goethite and hematite [40, 42].

Shown in Figure 6(a) is the transmittance spectrum of a ferric oxide OME. The transmittance is near zero in the ultraviolet region and increased to near unity in the near-IR region. At longer wavelengths some of the transmission loss can be attributed to light scattering by the film.

The photocurrent efficiency of the ferric oxide OMEs was evaluated in two- and three-electrode arrangements in aqueous electrolytes at pH 9.5. The incident photon-to-current efficiencies (IPCEs) were calculated with

$$\text{IPCE} = \frac{[1240 \text{ eV nm}][\text{photocurrent density } (\mu\text{A cm}^{-2})]}{[\text{wavelength (nm)}][\text{irradiance (mW cm}^{-2})]} \quad (1)$$

Here the photocurrents were measured on OMEs of known area with a potentiostat or an electrometer. The irradiance was quantified with a calibrated silicon photodiode in the same arrangement.

Shown in Figure 6(a) is the IPCE recorded as a function of the excitation wavelength, a photocurrent action spectrum, measured under short circuit conditions. The maximum observed IPCE was $0.7 \pm 0.1\%$ at 370 nm. This value is likely an underestimation of the true photocurrent yield, because no corrections were made for light absorption and scattering by the FTO substrate. The IPCE tailed into the visible region with no measurable photocurrent response at wavelengths longer than 600 nm.

The gradual increase in the photocurrent magnitude with increasing photon energy is typical of indirect semiconductors. For an indirect band gap semiconductor:

$$\text{IPCE} \cdot h\nu = A(h\nu - E_g)^2, \quad (2)$$

FIGURE 2: (a) Cross section and (b) plan view SEM image of a colloidal crystal template formed from 500 nm polystyrene (PS) particles.

FIGURE 3: (a) A plan view ESEM image of an electrodeposited ferric oxide OME surface fabricated by deposition into a colloidal crystal assembled from 0.5 μm diameter polystyrene particles. Inset: OME at higher magnification. (b) An SEM image of a cross section of a ferric oxide OME.

where $h\nu$ is the excitation energy, A is a constant, and E_g is the band gap [3, 43]. Figure 6(b) shows a plot of $[IPCE \cdot h\nu]^{1/2}$ versus $h\nu$ illustrating linear behavior over a wide range of photon energies. The band gap was obtained from extrapolation of the linear region. For a large number of samples the band gap was determined to be $E_g = 1.85 \pm 0.05$ eV.

Shown in Figure 7 are current-voltage curves for the OMEs in the dark and under illumination. Data are shown in the presence and absence of formate ion. The difference between the current collected in the dark and under illumination was the photocurrent. The photocurrents in the presence and absence of formate were converted to IPCEs to correct for differences in electrode area and light intensity. The observed IPCE was nearly twice as large in the presence of formate as in its absence for all potentials where measurable photocurrents were observed.

4. Discussion

The electrodeposition of ferric oxides into colloidal crystal templates has been successfully achieved for the first time.

Removal of the colloidal templates resulted in ordered macroporous electrodes (OMEs) that were utilized for photoassisted electrochemical oxidation. Our results suggest a possible new direction toward the realization of efficient charge capture from excitation of iron oxides with solar photons.

Environmental scanning electron microscopy revealed ferric oxide OME materials with architectures that would be expected based on the inverse structure of the colloidal templates. Infrared studies and X-ray diffraction data did not clearly match a known phase of ferric oxide [39, 40, 42]. The diffraction pattern showed peaks that were consistent with the major diffraction lines for a mixture of goethite and hematite, which represent the two most common polymorphs of ferric oxide [40, 44]. Very minor spectroscopic changes were observed after heat treatments at 300°C, conditions where crystalline ferric oxides, such as α -FeO(OH), β -FeO(OH), and γ -FeO(OH), and ferrihydrite, are known to be converted to the more thermodynamically stable hematite [40]. The stability of the ferric oxide OMEs to elevated temperature is surprising and could be exploited for additional processing steps such as the deposition of oxygen evolution catalysts.

FIGURE 4: ATR-FTIR spectra of an electrodeposited ferric oxide OME like that in Figure 2 before (solid) and after (dotted) annealing at 300°C.

FIGURE 5: X-ray diffraction pattern of an electrodeposited ferric oxide OME. Also shown for comparison are the peaks for goethite (open circles) and hematite (closed squares) crystals using Cu-K α radiation [40].

When utilized in alkaline aqueous photoelectrochemical cells the ferric oxide OMEs yielded a small sustained photocurrent. The direction of the current was consistent with an oxidation reaction at the illuminated OME and n-type behavior [8]. Under short-circuit conditions the maximum incident photon-to-current (IPCE) efficiency was $0.7 \pm 0.1\%$. Due to low photocurrent densities, no attempts were made to quantify if the photocurrent was from the formation of oxygen. Photocurrent action spectra revealed a maximum at about 370 nm that tailed into the visible region. A photocurrent was measured with green light and wavelengths >500 nm. Analysis of the photocurrent action spectra revealed an indirect band gap of 1.85 eV. This is significantly smaller than that measured for other

FIGURE 6: (a) A comparison of the short circuit incident photon-to-current efficiency (IPCE, squares) of a ferric oxide OME in 0.1 M NaCl at pH 9.5. Also shown is the transmittance spectrum (1-T, dashes) of the same material in air. (b) Band gap analysis of the IPCE.

FIGURE 7: Current-voltage curves of electrodeposited ferric oxide OMEs in 0.5 M Na₂SO₄ (squares) and 0.5 M Na₂SO₄ with 0.1 M NaCHOO (triangles). The data were measured in the dark (closed) and under illumination (open) with 20 mW/cm² of 413 nm light excitation.

ferric oxides, Table 1, and is nearly ideal for water splitting applications [40, 44]. The comparatively small band gap allows for more efficient solar photon harvesting by the OME than by other ferric oxide phases.

In a 3-electrode photoelectrochemical cell, a gradual increase in the photocurrent was observed as the applied potential was increased. The addition of formate to the electrolyte resulted in an approximate doubling of the magnitude of the photocurrent. It is known that the one electron oxidation of formate produces a highly energetic radical that can inject electrons into the conduction band of some semiconductors, effectively doubling the current [45, 46]. Kennedy and Frese have previously suggested that

TABLE 1: Band Gaps of Common Ferric Oxides.

Ferric Oxide	E_g (eV)	References
Hematite	2.20	[40, 44]
Goethite	2.10	[40, 44]
Akaganeite	2.12	[40, 44]
Lepidocrocite	2.06	[40, 44]
Ferric Oxide OME	1.85	here

current doubling occurs at illuminated hematite electrodes [15] and these results indicate that it also present with ferric oxide OMEs. At potentials greater than +1.2 V versus Ag/AgCl a dark oxidation current increased dramatically so that such positive excursions were avoided.

Small photocurrents observed at hematite single crystal and thin film electrodes have previously been attributed to short minority carrier (hole) diffusion lengths [6]. In previous work, ordered arrays of hematite nanorods were employed to minimize the distance holes that travel to reach the aqueous interface. Indeed, an increased photocurrent efficiency was observed [30, 47]. In principle, a benefit of ordered nanorod arrays over the OMEs studies here is the direct path for electron transport to the current collector that minimizes transit time by reducing lateral electron transport. On the other hand, high aspect ratio nanorod or nanowire arrays tend to be fragile with no lateral connectivity to provide the structural support present in the interconnected porous architecture of OMEs.

The largest solid features in the ferric oxide OME reported here come from the tetrahedral and octahedral sites in the colloidal crystal template [38]. The tetrahedral sites are formed from four spheres where the centers of the spheres form a tetrahedron. Equivalently, the tetrahedral site results from a sphere that occupies a threefold hollow site on a close packed plane. The octahedral sites are formed from six spheres and correspond to the unoccupied threefold hollow sites in the close-packed planes. For the OMEs fabricated here with 500 nm particles as templates, the diameters of the large solid regions, corresponding to the largest spheres that can fit into the tetrahedral and octahedral sites. These are 113 nm and 207 nm, respectively [38]. Thus the longest distances for carrier diffusion in these structures are 57 nm and 104 nm. Kennedy and Frese reported hole diffusion lengths of 2–4 nm [15], while Dare-Edwards et al. found them to be somewhat larger, 20 nm [9]. This photoelectrochemical data is consistent, at least qualitatively, with the short lifetimes of electron-hole pairs photogenerated in colloidal hematite solutions [48].

If the hole diffusion lengths reported for hematite are relevant to the ferric oxide OMEs, a significant fraction of holes would not reach the aqueous interface to form oxygen-oxygen bonds. This likely explains the low photocurrent efficiency observed. In future work could be rigorously tested with the methodology developed here but with smaller beads as templates. We note that 20 nm beads are commercially available and are predicted to yield ferric oxide OMEs with solid features only 2–4 nm in radius. This is very close to the

hole diffusion length estimated for hematite and would be expected to increase the solar conversion efficiency for water splitting.

5. Conclusion

The electrodeposition of ferric oxides into colloidal crystal templates was successfully achieved. The resultant ordered macroporous electrodes were about 2 microns thick with the inverse structure of the colloidal templates. Spectroscopic characterization did not match a known phase of ferric oxide but suggested a mixture of goethite and hematite. The photocurrent action spectra in the visible region revealed a more favorable band gap (1.85 eV) than known polymorphs of ferric oxide. However, the photocurrents were disappointingly small, even with a substantial positive applied potential. Holes that were photogenerated in the centers of octahedral and tetrahedral sites within these ordered macroscopic electrodes must traverse hundreds of nanometers to reach the aqueous interface. Charge recombination likely limits the hole diffusion length and therefore represents a significant loss mechanism in the solar energy conversion efficiency. While the efficiency toward practical water splitting was disappointing for these specific ferric oxide mesoporous electrodes, the ability to synthesize finely tuned architectures on the nanometer length scale provides exciting new opportunities for future energy applications.

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